RESEARCH ARTICLE

Synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by Perchlorated Zirconia (HClO4/ZrO2) nanoparticles as a novel solid acid catalyst

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Abstract: Aim: Zirconia was synthesized in nanosize by sol-gel method and perchlorated zirconia (HClO4/ZrO2) with various calcination temperatures were prepared and characterized by XRD, FTIR and SEM techniques. The catalyst acidity characters, including the acidicstrength and the total number of acid sites were determined by potentiometric titration. The catalytic performance experiments show that the HClO4/ZrO2 with calcination temperature of 300 °C has the best catalytic activity. 2,3-Dihydroquinazolin-4(1H)-ones were prepared in good to excellent yields via condensation reaction of oaminobenzamide and various types of aldehydes and ketones in the presence of HClO4/ZrO2 nanoparticles as an efficient solid acid catalyst. The catalyst is reusable with moderate loss in activity.

Keywords: Perchlorated Zirconia; Nanoparticles; 2,3-Dihydroquinazolin-4(1H)-ones; Solid acid catalyst; Reusability

1. Introduction

2,3-Dihydroquinazolinones and their derivatives have recently attracted considerable attention because of their potential biological and pharmaceutical activities including antibacterial[1]., anticancer[2]., antifungal[3]. anticonvulsant and calcium channel blocking activities[4-7].. Additionally, these compounds can be oxidized to their corresponding quinazolin-4(1H)-ones, an important class of biologically active compounds[8]. Several synthetic methodologies for the synthesis of these compounds have been reported using various reactants and catalysts. Among them, the general method includes condensation reaction of o-aminobenzamide with an aldehyde or ketone using acid catalysts, such as ZrCl4[9]., TBAB[10]., NH2SO3H [11]., H3PW12O40[12]., Poly(4-vinylpyridine) [13]., trichloroacetic acid[14]. and succinimide-N-sulfonic acid [15].. However, many of these methods, have limitations such as long reaction times, harsh reaction conditions, expensive and large amount of the catalyst, low yields, tedious workup and high reaction temperature. Therefore, the development of mild, simple, clean, high-yielding and efficient processes for the synthesis of these important compounds are still desirable and are in demand. In recent years, zirconia has attracted considerable attention as both catalyst and catalyst support because of its interesting properties such as high thermal stability and the amphoteric character of its surface hydroxyl groups[16,17]. Zirconia is widely used as a catalytic support or promoter in numerous reactions because of its moderate acidity and basicity, high thermal stability, and surface oxygen mobility and It is the only known oxide believed to possess acidic, basic and redox properties altogether[18-21]. Zirconia modified with inorganic materials has been used as strong solid acid catalyst in many organic transformations[22-24].

In continuation of our efforts to develop the use catalysts in organic transformations[25-27]., herein, we report synthesis, characterization and catalytic application of perchlorated zirconia(HClO4 /ZrO2) for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the reaction of o-aminobenzamide and aldehydes or ketones (Scheme 1).

doi: 10.18686/nn.v1i1.

2. Experimental

2.1 Materials and methods

All chemicals were commercial products. All reactions were monitored by TLC and all yields refer to isolated products. Melting points were obtained by Buchi B-540 apparatus and are uncorrected. 1H and 13C NMR spectra were recorded in DMSO-d6 on a Bruker (AVANCE) 500 MHz and 400 MHz spectrometer. Infrared spectra of the catalysts and reaction products were recorded on a Bruker FT-IR Equinax-55 spectrophotometer. XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using nickel filtered Cu Kα radiation (λ = 1.5406 Å). The morphology was studied using a Philips XL30 scanning electron microscopy. The catalyst acidity characters, including the acidic strength and the total number of acid sites were determined by potentiometric titration.

2.2 Preparation of perchlorated zirconia (PZ)

Nanosized zirconia was prepared by sol-gel method using ZrCl4 as Zr source. The HClO4/ZrO2 was prepared by impregnation of ZrO2 using HClO4 and dried at 120 °C to obtain HClO4/ZrO2 denoted as PZ-120. The PZ-120 was calcined at 200, 300, 400 and 500 °C for 4 h and the obtained samples were denoted as PZ-200, PZ-300, PZ-400 and PZ-500, respectively. ZrCl4 (5.6 g) was dissolved in deionized water (200 mL) and to this solution, dilute aqueous ammonia (NH4OH, 5%) was added drop-wise under vigorous stirring until the pH of the solution reached to 9.5. The obtained Zr(OH)4 gel was stirred for 24 h, centrifuged, then washed with distilled water until free from chloride ions and dried at 120 ºC for 12 h. The uncalcined hydroxide gel (Zr(OH)4) was perchlorated by stirring in 1M HClO4 (15 mL/g) for 24 h. The solid was separated by centrifuge and washed with EtOH, dried at 120 ºC for 4 h and calcined at 300 ºC for 4 h to obtain PZ-300 nanoparticles. General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones. To a solution of o-aminobenzamide (1 mmol) and aldehyde (1.2 mmol) in EtOH (1.5 mL), HClO4/ZrO2 (50 mg) was added. The mixture was stirred under reflux condition for an appropriate time. After completion of the reaction, as indicated by TLC, hot EtOH (2 mL) was added to the reaction mixture and then the precipitate was filtered off and washed with EtOH and water. Finally the crude product was purified by recrystallization from EtOH and water to afford the corresponding 2,3-dihydroquinazolin-4(1H)-ones in good yields (80–98%).

2.3 Physical and spectroscopic data for selected compounds

3a: White solid; FT-IR: υmax (neat) = 3303 (NH), 3176 (NH) and 1651 (C=O) cm-1; 1H NMR (500 MHz, DMSO-d6): δ (ppm) = 5.76 (s, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 7.10 (brs, 1H, NH), 7.25 (t, J = 7.3, 1H), 7.33-7.41 (m, 3H, ArH), 7.50 (d, 2H, J = 7.4 Hz, ArH), 7.62 (d, J = 7.8 Hz, 1H), 8.28 (brs, 1H, NH); 13C NMR (125 MHz, DMSO-d6): δ(ppm) = 67.43, 115.26, 115.83, 117.97, 127.72, 128.21, 129.18, 129.31, 134.16, 142.51, 148.73, 164.45.

3b: White solid; FT-IR: υmax (neat) = 3297 (NH), 3176 (NH) and 1651 (C=O) cm-1; 1H NMR (500 MHz, DMSO-d6): δ (ppm) = 3.75 (s, 3H), 5.71 (s, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H, ArH), 7.00 (brs, 1H, NH), 7.24 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 8.6 Hz, 2H, ArH), 7.62 (d, J = 7.7 Hz, 1H), 8.17 (s, 1H, NH); 13C NMR (100 MHz, DMSO-d6): δ (ppm) = 67.17, 114.51, 115.28, 115.88, 117.95, 128.21, 129.07, 134.09, 134.35, 148.88, 160.30, 164.55.

3c: White solid; FT-IR: υmax (KBr) = 3311 (NH), 3132 (NH) and 1654 (C=O) cm-1; 1H NMR (400 MHz, DMSO-d6): δ 2.29 (s, CH3,3H), 5.70 (s, CH,1H), 6.64-6.68 (m, 1H, ArH), 6.77 (d, J = 8.0, 1H, ArH), 7.06 (brs, NH, 1H), 7.19 (d, J = 8.0, 2H, ArH), 7.21-7.25(m, 1H, ArH), 7.37(d,J = 8.0, 2H, ArH), 7.604 (d, J = 9.2, 1H, ArH), 8.24 (brs, NH, 1H); 13C NMR (100 MHz, DMSO-d6): δ 20.8, 66.3, 114.9, 117.0, 120.8, 127.6, 129.8, 141.4, 147.8, 163.5.

3d: White solid; FT-IR: υmax (KBr) = 3307 (NH), 1653 (C=O) cm-1; 1H NMR (400 MHz, DMSO-d6): δ 5.77 (s, CH, 1H), 6.68-6.70 (m, 1H, ArH), 6.74 (d, J = 8.4, 1H, ArH), 7.15 (br, NH, 1H), 7.23-7.27 (m, 1, ArH), 7.46 (d, J = 8.4, 2H, ArH), 7.51 (d, J = 8.8, 1H, ArH), 7.62 (d, J = 5.6, 1H, ArH), 8.34 (s, NH, 1H); 13C NMR (100 MHz, DMSO-d6): δ 65.7, 114.4, 114.8, 117.2, 127.3, 128.2, 128.6, 133.3, 134.6, 140.6, 147.6, 163.4.

3e: Yellow solid, FT-IR: υmax (KBr) = 3286 (NH), 3190 (NH) and 1647 (C=O) cm-1; 1H NMR (400 MHz, DMSO-d6): δ 5.91 (s, CH, 1H), 6.67-6.71 (m, 1H, ArH), 6.77 (d, J = 8.4, 1H, ArH), 7.24-7.28 (m, 1H, ArH), 7.34 (brs, NH, 1H), 7.60-7.62 (1H, ArH), 7.74 (d, J = 9.2, 1H, ArH), 7.62 (d, J = 5.6, 1H, ArH), 8.34 (brs, NH, 1H) ; 13C NMR (100 MHz, DMSO-d): δ 65.2, 114.5, 114.8, 123.5, 117.4, 127.3, 127.9, 133.5, 147.1, 147.3, 149.2, 163.4 .

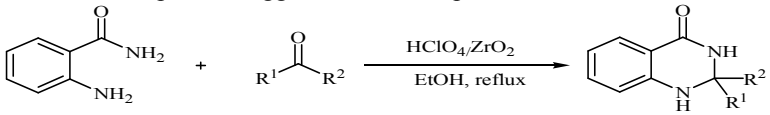
3h: White solid; FT-IR: υmax (neat) = 3356 (NH), 3181 (NH) and 1656 (C=O) cm-1; 1H NMR (400 MHz, DMSO-d6): δ (ppm) = 3.75 (s, 3H, MeO), 3.76 (s, 1H, MeO), 5.71 (s, 1H), 6.67 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.94-7.03 (m, 2H,), 7.04 (s, 1H, NH), 7.15 (d, , J = 2.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 8.22 (s, 1H, NH); 13C NMR (100 MHz, DMSO-d6): δ (ppm) = 55.40, 55.51, 66.52, 110.52, 111.16, 117.12, 119.19, 127.31, 133.22, 133.49, 148.05, 148.53, 148.94, 163.74.

3j: White solid; FT-IR: υmax (neat) = 3286 (NH), 3161 (NH) and 1643 (C=O) cm-1; 1H NMR (500 MHz, DMSO-d6): δ (ppm) = 1.65-1.67 (m, 4H), 1.74-1.81 (m, 4H), 6.62 (t, J = 7.7 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.73 (brs, 1H, NH), 7.20 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 8.07 (brs, 1 H, NH) ; 13C NMR (125 MHz, DMSO-d6): δ (ppm) = 22.85, 40.16, 77.94, 115.21, 115.46, 117.41, 128.11, 133.87, 148.39, 164.31.

3. Results and Discussions

3.1 The catalyst characterization

The FT-IR, SEM, XRD and potentiometric titration techniques were applied for the characterization of samples. The SEM image of PZ-300 shows spherical agglomerated nanoparticles with the size of less than 100 nm **Figure 1.**



Scheme 1. The synthesis of 2,3-dihydroquinazolin-4(1H)-ones by $HClO_4/ZrO_2$) nanoparticles

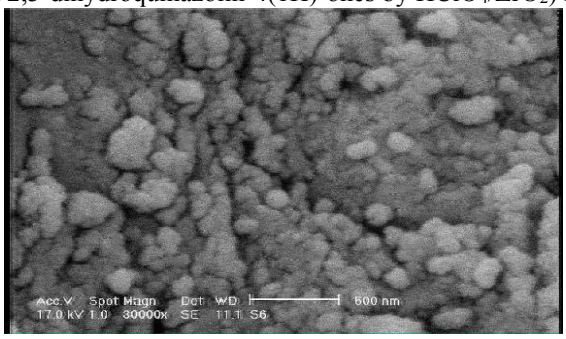


Figure 1; SEM image of HClO4/ZrO2

To confirm the presence of perchlorate anion on the zirconia, FT-IR spectra of PZ-300 was compared to that of ZrO_2 **Figure 2.** The spectrum of PZ-300 shows characteristic peaks of perchlorate groups of different symmetry at 1203, 1153, 1084, 952 and 632 cm^{-1}[26].. The sharp peak at 1423 cm^{-1} is assigned to Cl=O vibration of perchlorate group.

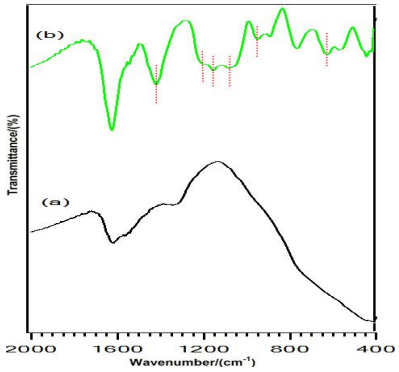


Figure 2; FT-IR spectra of (a) ZrO2, (b) PZ-300

The morphology of zirconia and the effect of perchlorate on the crystalline phase of zirconia were studied by XRD technique and results are shown in **Figure 3.** XRD patterns of PZ-100, PZ-200 and PZ-300 show amorphous structure for zirconia in the samples. As shown in the XRD patterns of PZ-400 and PZ-500 (Figure 3d and 3e), at higher calcination temperature, mixture of monoclinic and tetragonal phases of zirconia were formed with the later as major constituent. These results confirm that, the same as other modifiers, perchlorate cannot stabilize tetragonal phase of zirconia.

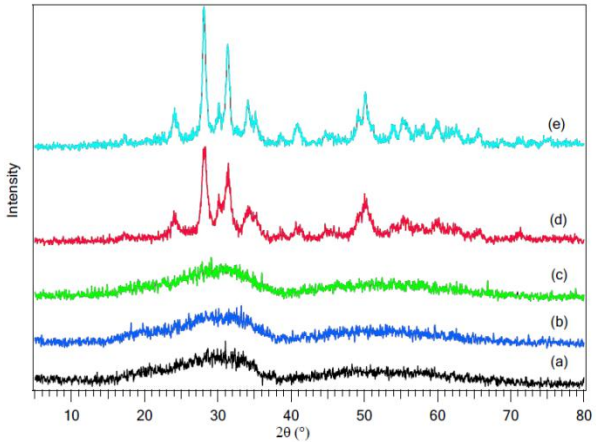


Figure 3; XRD patterns of HClO4/ZrO2 calcined at a) 100 °C, b) 200 °C, c) 300 °C, d) 400

According to the ZrO_2 phase diagram (figure 4). Zirconia has 3 crystal structure: monoclinic, tetragonal and cubic, which are stable in range of 0-1205 C, 1205-2377 C and 2377-2710 C respectively. In this study we have achieved to the mixture of tetragonal and monoclinic structure by perchlorating of zirconia in 400 C and 500 C.°C and 500 °C

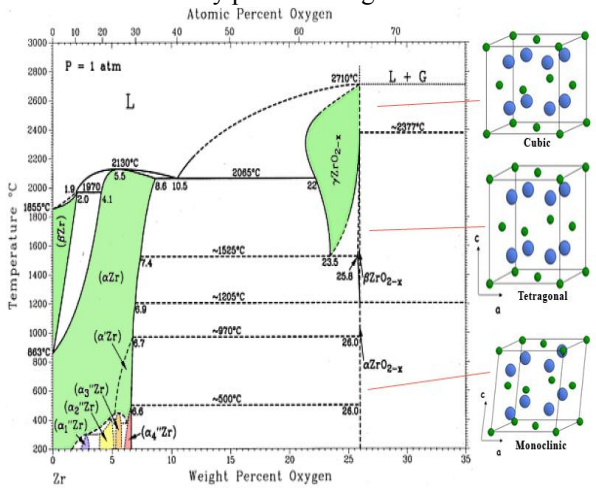


Figure 4; ZrO2 phase diagram

The catalyst acidity characters of PZ calcined in various temperature, including the acidic strength and the total number of acid sites, were determined by potentiometric titration. According to this method, the initial electrode potential (E) indicates the maximum acid strength of the surface sites and the range where a plateau is reached (meq/g) indicates the total number of acid sites. Therefore, a suspension of the catalyst in acetonitrile was potentiometrically titrated with a solution of n-butylamine in acetonitrile. As shown in **Figure 5**, very low initial potential shows that PZ400 and PZ500 are very weak acid relative to PZ300. The pattern 4c and 4b also show that the initial potential of -4 and 34 mV reache to a value of -31 mV for 0.1 and 0.4 meq/g respectively, while in the pattern of 4a initial potential of 370 mV reaches to a value of -31 mV for 0.8 meq/g. This confirms the presence of higher number of acid sites on the PZ300. Also according to the diagram and higher initial electrode potential of PZ300(E> 370mv) compared to PZ400 and PZ500 it is clear that the acidic strength of PZ300 is very higher than PZ400(E<34mv) and PZ500(E<-4 mv).

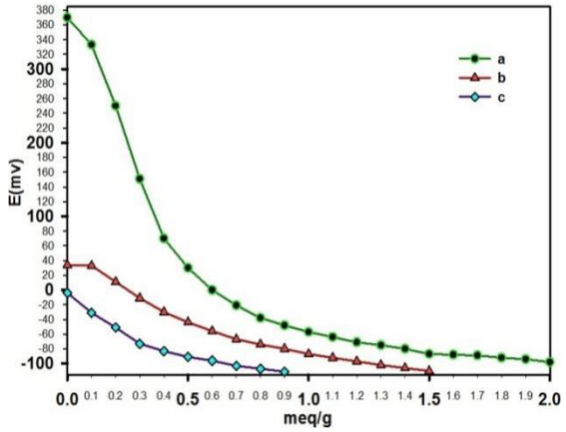


Figure 5; Potentiometric titration curves of PZ300(a), PZ400(b), PZ500(c)

3.2 The catalyst activity

The catalytic activity of $HClO_4$/ ZrO_2 was investigated in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the reaction of o-aminobenzamide with aldehydes or ketones. Initially, the optimization experiments were performed in the reaction of o-aminobenzamide (1 mmol) and benzaldehyde (1 mmol) as the model reaction and the results are shown in Table 1. To investigate the effect of calcination temperature on the catalytic activity of $HClO_4/ZrO_2$, the model reaction was performed in the presence of 100 mg of various PZ samples, prepared in 2 M concentration of $HClO_4$, and results show that PZ-300 has the best activity based on reaction time (Fig.6). To obtain the best concentration of $HClO_4$ for the preparation of PZ, the model reaction in the presence of 100 mg PZ-300, prepared in 1, 2 and 3 M concentration of $HClO_4$, was also performed and according to the results shown in Fig. 6, the best catalytic activity was achieved in 1 M concentration of $HClO_4$.

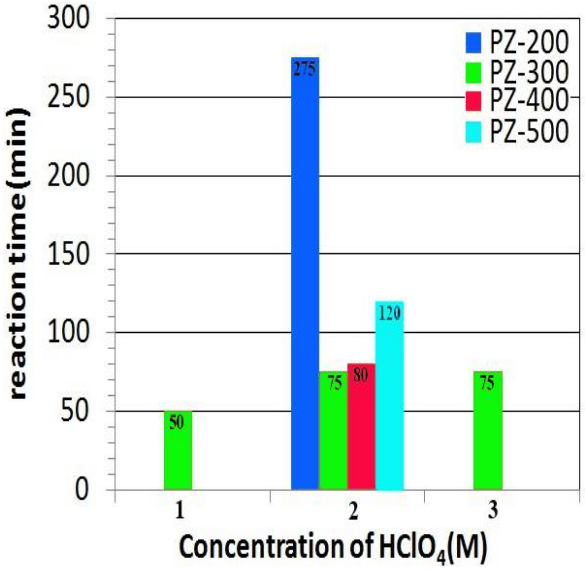


Figure 6; Reaction of o-aminobenzamide with benzaldehyde in the presence of HClO4/ZrO2 (100 55mg) prepared in various calcination temperatures and various concentrations of HClO4 in EtOH at reflux condition

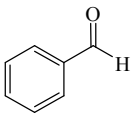
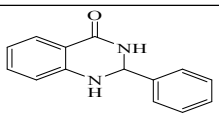
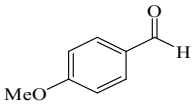
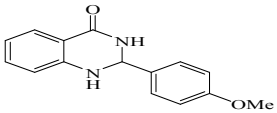
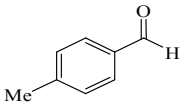
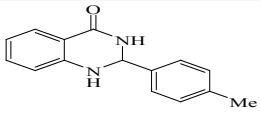
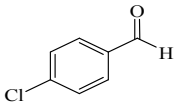
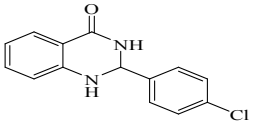
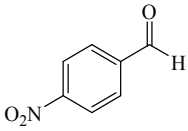
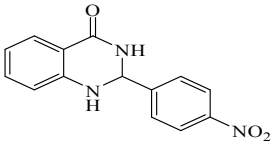
To optimize amount of the catalyst, the model reaction was performed in the presence of various amounts of PZ-300 (Table 1). The results show that in terms of reaction times and yields of the products, 50 mg of PZ-300 has the best activity for the reaction of 1 mmol reactants (Table 1 entry 4).

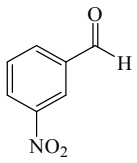
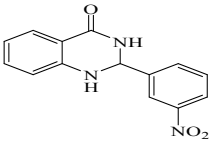
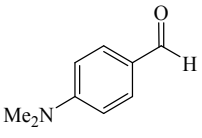
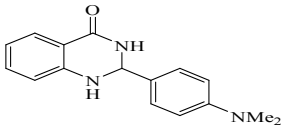
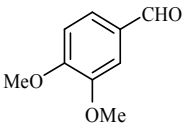
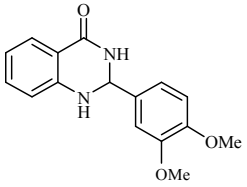
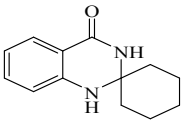
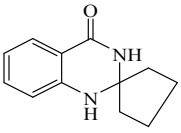
To study the effect of solvent on the condensation reaction, the model reaction was carried out in the presence of various solvents. The results show that in terms of times and yields, EtOH was the best choice for this reaction (Table 1, entry 4). To show the efficiency of the perchlorate on the catalytic activity of PZ, the model reaction was carried out in the presence of 50 mg ZrO under the same reaction conditions. And low yield of the product was obtained.

Entry	PZ-300 (mg)	Solvent	Time(min)	Yield(%)
1	150	EtOH	35	74
2	100	EtOH	50	77
3	75	EtOH	65	84
4	50	EtOH	70	89
5	25	EtOH	120	73
6	50	MeOH	65	65
7	50	CH_3CN	70	10
8	50	EtOAc	240	53
9	50	CH_2Cl_2	70	10
10	50	CCl_4	70	5

Table 1. Reaction of o-aminobenzamide with benzaldehyde in the presence of various amounts of PZ-300 and various solvents.

Following the obtained results, the reaction of o-aminobenzamide and various aldehydes with both electron-donating and electron-withdrawing substituents were carried out in the presence of 50 mg PZ-300 in EtOH at reflux condition and the corresponding 2,3-dihydroquinazolin-4(1H)-ones were obtained in good yields (Table 2, entry 3a-h). Cyclic ketones were also reacted with o-aminobenzamide and the corresponding 2,3-dihydroquinazolin-4(1H)-one with spiro structure were obtained in good yields at short reaction times (Table 2, entries 3i and 3j).

Entry	Aldehyde or ketone (2)	Dihydroquinazolinone(3)	Time (min)	Yield (%)	M.P.	
					(Found)	(Reported)
A			70	89	227-229	218-219[24]
B			60	80	191-194	192-193[24]
C			75	90	232-233	233-234[24]
D			90	95	203-207	205-206[24]
E			155	81	202-204	213-214 [24]

F			260	80	201-203	216-217 [24]
G			155	88	208-211	228-229 [24]
H			55	82	213-217	210-213[25]
I			55	98	6-228	224-225[13]
J			30	91	257-259	257-260[12]

Tabel 2. Synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the reaction of o-aminobenzamide with aldehydes or ketones in the presence of 50 mg HClO4/ZrO2 in EtOH at reflux condition.

To investigate reusability of the catalyst, the recovered catalyst from the model reaction was washed with EtOH, dried at 120 °C for 2 h and used in the same reaction. The results show moderate decrease in catalytic activity (Table 3, run 2). The recovered catalyst from run 2, was washed with EtOH and calcined at 300 ºC for 2 h. The catalyst was then used in the model 3 reaction and result shows increase in catalytic activity to nearly the same value as that of the fresh catalyst (Table 3, run 3). This result indicates partial blockage of surface of the catalyst after each run.

Run	Time (min)[a]
1	70
2	125
3	85

[a]Time for 100% conversion of reactant

Table 3. Reusability of PZ-300 in the reaction of o-aminobenzamide with benzaldehyde.

Finally we compared our catalyst with other catalysts. According to the results shown in table 4, it is clear that $ZrCl_4$ has the best reactivity compared to other catalysts but due to the its non-reusability , PZ300 is better than $ZrCl_4$ and also in terms of yield and reaction time PZ300 is also comparable with other catalysts.

Entry	**Catalyst**	**Amount of catalyst(mg)**	**Reaction condition**	**Time (min)**	**Yield(%)**
1	PZ300	50	In EtOH , at 80° C	70	89
2	$ZrCl_4$	4	In EtOH, room temperature	25	93
3	SiO_2-$FeCl_3$	5	Solvent-free, at 80° C	360	87

4	SO_4^{2-}/ZrO_2	40	In EtOH, at 80° C	30	92

Table 4. Compersion of PZ300 with other catalysts

4. Conclusion

In conclusion, we introduced HClO4/ZrO2 as novel solid acid catalyst for efficient synthesis of 2,3-dihydroquinazolin-4(1H)-ones. High yield of the products, ease of workup, simple purification and green condition makes this method attractive for the synthesis of 2,3- dihydroquinazolin-4(1H)-ones.

Acknowledgements

We are thankful to the Payame Noor University of Ardakan for financial support of this work.

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